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FINAL DRAFT

Overview of PNGV Battery Development and Test Programs

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ABSTRACT

Affordable, safe, long-lasting, high-power batteries are requisites for successful commercialization of hybrid electric vehicles. The U.S. Department of Energy's Office of Advance Automotive Technologies and the Partnership for a New Generation of Vehicles are funding research and development programs to address each of these issues. An overview of these areas is presented along with a summary of battery development and test programs, as well as recent performance data from several of these programs.

INTRODUCTION

Lightweight, compact, high-power energy storage devices are critical enabling technologies for a viable hybrid electric vehicle (HEV) propulsion system. Successful commercialization of HEV's requires improvements in a number of technological areas including electrochemical energy storage. To address all of these areas, a cooperative research and development (R&D) program called the Partnership for a New Generation of Vehicles (PNGV) was formed in 1993 between the Federal Government and the U.S. Council for Automotive Research (USCAR), whose members are DaimlerChrysler, General Motors, and Ford Motor Company (Ref. 1). Major objectives of the program are to develop technologies for a new generation of HEV's with fuel economies up to three times (80 miles per gallon) the average family sedan. At the same time, these vehicles should maintain performance, size, utility, and cost of ownership, and meet federal safety and emissions requirements.

As detailed in References 2 and 3, the U.S. Department of Energy's (DOE) Office of Advanced Automotive Technologies (OAAT) is

sponsoring several programs aimed at the development of batteries for HEV applications. This includes both participation in the PNGV Program which is developing prototypical cells, modules, and full-size automotive battery packs, as well as more fundamental R&D programs that are investigating new materials, components, and basic chemical and electrochemical phenomena. As such, it relies on a broad spectrum of contributors including several federal agencies, automobile manufacturers, battery developers and suppliers, national laboratories, and university organizations.

Coordination between federal agencies is accomplished through the government-sponsored Interagency Advance Power Group. To facilitate integration of high-power batteries into hybrid vehicles, OAAT's Vehicle High-Power Energy Storage Program works with the DOE Vehicles Systems Teams to coordinate efforts in modeling, hardware evaluation, and system integration. Calendar life, abuse tolerance, and cost issues are being addressed by OAAT's Advance Technology Development (ATD) Program. And lastly, the investigation of new electrochemistries that offer the potential for improvements in advanced batteries is conducted under the auspices of OAAT's Batteries for Advanced Transportation Technologies (BATT) Program. These programs form an integrated approach to addressing the challenges of cost, safety, life, and power.

OAAT and PNGV R&D Programs

For completeness, the BATT and ATD research and development programs are first briefly described, but the emphasis of this paper is the PNGV battery development and test program. Then, using recent performance data from the ATD program and from several different Saft America, Inc. (Saft) batteries as examples, this paper concludes with a description of PNGV

analysis methodologies including several new approaches to life modeling.

Batteries for Advance Transportation Technologies

High cell potentials and demanding cycling requirements have led to chemical and mechanical instabilities. The OAAT's Batteries for Advance Transportation Technologies Program is addressing these important issues. This program, which was formerly known as the Exploratory Technology Research (ETR) Program, is managed by Lawrence Berkeley National Laboratory (LBNL), with the active involvement of other national laboratories, universities, and industrial organizations.

The eight primary BATT Program task areas are: (1) optimized lithium-ion systems, (2) high-performance non-flammable electrolytes, (3) non-carbonaceous anode materials, (4) novel cathode materials, (5) advanced solid polymer electrolytes, (6) advanced diagnostic methods, (7) improved electrochemical models, and (8) novel electrode couples. Reference 4 provides details of the BATT Program, its activities, and recent accomplishments.

Advanced Technology Development

In 1998, the OAAT initiated the Advanced Technology Development (ATD) Program to address key technical barriers to the commercialization of lithium-ion batteries for HEV applications (Ref. 5). These barriers are calendar life, abuse tolerance, and cost. To reduce the R&D risk to the U.S. auto companies associated with overcoming these obstacles, OAAT in conjunction with the PNGV Electrochemical Energy Storage Technical Team has established support programs at DOE's national laboratories in the following five areas:

- Cell development and evaluation: Argonne National Laboratory (ANL), Idaho National Engineering and Environmental Laboratory (INEEL), and Sandia National Laboratories (SNL)
- Electrochemistry diagnostics evaluations: LBNL, ANL, Brookhaven National Laboratory (BNL), SNL, and INEEL
- Electrochemistry improvement: ANL
- Low-cost cell packaging: ANL
- Advanced process research: ANL

PNGV BATTERY DEVELOPMENT

The primary functions of the high-power energy storage device are to load-level the demand on the prime power source; maximize efficiency and minimize engine weight, volume, and cost; recapture the vehicle kinetic energy through regenerative braking; and capture the energy from the prime power source during idle periods. In contrast to EV's, the energy storage device needed for HEV's must have high specific power; that is, the power-to-energy ratio must be greater than 25 W/Wh, as opposed to 2-3 W/Wh for EV's. The objective is to develop a low-cost, high-power energy storage device that meets or exceeds the energy storage requirements for the Power Assist and the Dual Mode HEV by 2008. In general, the Dual Mode concept requires that the battery supplies a larger fraction of the overall HEV power and energy needs than for the Power Assist concept. Hence, the Dual Mode power and energy goals are considerably higher than the Power Assist goals. In both cases, the life goal is 15 years.

Since 1993, PNGV has been working with battery developers on a cost-sharing basis to investigate and develop new technologies that show promise towards meeting the PNGV cost and performance goals. Recently participating battery suppliers, their responsibilities, and progress through FY 2000 are shown in Table 1.

The success of the PNGV battery development program may be further measured by its major accomplishments, which are listed below:

- The initial evaluation of alternative technologies has been completed. Results indicate that NiMH shows promise for lower cost and stable life. Lithium-polymer systems are still under evaluation.
- Lithium-ion calendar life was improved 50%. Also, a full-size automotive pack with electronic control and thermal management systems successfully completed the PNGV goal of 300,000 Power Assist life cycles. Efforts continue to further improve life, abuse tolerance, and cost.
- A NiMH and a Li-Ion Phase II program for 50-V module demonstrations were completed. Each delivered 50-V modules.

FINAL DRAFT

Table 1. FY 2000 PNGV battery suppliers and their responsibilities and progress (Ref. 3).

Participant	Responsibility	Progress
SAFT America, Inc.	Develop and demonstrate SAFT high-power battery technologies based on nominal 6- and 12-Ah lithium-ion cells at the nominal 50-V module level with electronic and thermal management	<ul style="list-style-type: none"> Delivered two full-scale hybrid battery systems Improved cell life capability to 10 years
VARTA	Develop and demonstrate VARTA high-power battery technologies using nominal 10-Ah NiMH cells at the nominal 50-V module level with electronic and thermal management	<ul style="list-style-type: none"> Developed low-cost modular design
PolyStor	Develop and demonstrate a 50-V, full-capacity lithium-ion module using a 8-Ah PolyStor cell design	<ul style="list-style-type: none"> Delivered 50-V modules Improved life capability to 7 years
Delphi	Benchmark and demonstrate that Delphi lithium-metal polymer technology can meet the technical targets	<ul style="list-style-type: none"> Adopted ATD materials
AVESTOR	Benchmark and demonstrate that AVESTOR lithium-metal-polymer technology can meet the technical targets	<ul style="list-style-type: none"> Demonstrated high-power capability
Texaco-Ovonic, Inc.	Benchmark and demonstrate that Texaco-Ovonic NiMH technology can meet the technical targets	<ul style="list-style-type: none"> Demonstrated 600 W/kg electrode stacks
Electro Energy, Inc.	Benchmark and demonstrate that Electro Energy bipolar NiMH technology can meet the technical targets	<ul style="list-style-type: none"> Demonstrated bipolar NiMH high-power configurations

- U. S. auto companies chose to pursue several advanced battery technologies: Saft Li-ion by DaimlerChrysler; VARTA NiMH by Ford; Texaco-Ovonic NiMH by General Motors; and AVESTOR Li-polymer by General Motors. These advanced battery technologies were featured in the PNGV concept cars unveiled in early 2000, namely, the DaimlerChrysler ESX3, Ford Prodigy, and GM Precept.
- Additional work was conducted to update the PNGV Test Procedures Manual (Ref. 6) to include a cold cranking test; adjust the hybrid pulse power cycle to reflect dual mode requirements; improve efficiency profiles; refine the dual mode cycle-life procedure; and assess thermal management energy consumption.

PNGV TEST AND EVALUATION

As PNGV battery suppliers develop new technologies, their batteries are sent to national laboratories for independent and objective test and evaluation.

To this end, PNGV Energy Storage system performance goals have been developed based on anticipated representative usage and

integration with other HEV system requirements. These goals are summarized in Table 2 for both the Power Assist and Dual Mode applications. To assess battery performance against the PNGV goals, a cadre of tests and analytical procedures has been developed, and is defined in detail in Reference 6 and summarized below.

In recent years, the investigation of energy storage devices for HEV's has focused on high-power lithium-ion, lithium polymer, and nickel metal hydride batteries, all of which are being tested at the INEEL. Prototypical batteries may range from laboratory- and full-size cells, to modules consisting of an ensemble of cells, to full-size batteries having electronic and thermal control systems.

Prior to starting any test sequence, all equipment is calibrated and all tests are closely controlled at prescribed states-of-charge (SOC), test profiles, and temperatures by using environmental chambers and programmable testers. A measurement and control study of the INEEL Energy Storage Laboratory testers has recently been completed, and has determined the uncertainty of both measured parameters (i.e., temperature, current, and voltage) and derived parameters (i.e., power, capacity, energy, impedance, efficiency, and self-discharge) (Ref.

FINAL DRAFT

Table 2. PNGV Energy Storage system performance goals.

Characteristics	Units	Power Assist	Dual Mode
Pulse discharge power	kW	25 (18 s)	45 (12 s)
Peak regenerative pulse power	kW	30 (2 s) (min 50 Wh over 10 s regen total)	35 (10 s) (97 Wh pulse)
Total available energy (over DOD range where power goals are met)	kWh	0.3 (at $C_1/1$ rate)	1.5 (at 6-kW constant power)
Minimum round-trip energy efficiency	%	90	88
Cold cranking power at -30°C (three 2-s pulses, 10-s rests between)	kW	5	5
Cycle life, for specified SOC increments	cycles	300,000 Power Assist cycles (7.5 MWh, total)	3,750 Dual Mode cycles (22.5 MWh, total)
Calendar life	years	15	15
Maximum weight	kg	40	100
Maximum volume	l	32	75 (at 165-mm max height)
Operating voltage limits (Note: Maximum current is limited to 217 A at any power level)	Vdc	max ≤ 440 min $\geq (0.55 \times V_{max})$	Max ≤ 440 min $\geq (0.5 \times V_{max})$
Maximum allowable self-discharge rate	Wh/day	50	50
Temperature range:			
Equipment operation	°C	-30 to +52	-30 to +52
Equipment survival		-46 to +66	-46 to +66

7). This information has been utilized to develop precise testing and measurement standards to ensure consistent and objective evaluation over the broad range of products tested in the laboratory.

Following receipt inspection of test articles, a series of characterization tests are performed. These tests include static capacity, pulse power, available energy, self-discharge, cold cranking, thermal performance, energy efficiency, and electrochemical impedance spectroscopy (EIS).

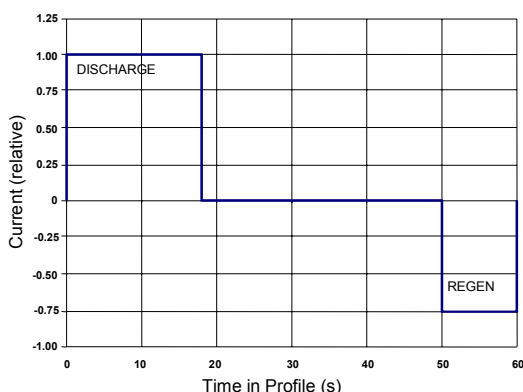
The static capacity test is a series of at least three complete $C_1/1$ discharges that are repeated until results agree within 2%. This demonstrates charge and discharge stability and helps condition the batteries for further testing.

Next, discharge and regen pulse powers are calculated (as described later in this paper)

utilizing the low-current Hybrid Pulse Power Characterization (L-HPPC) Test. Figure 1 shows a typical pulse power profile from the HPPC test. The L-HPPC test consists of a series of discharge and regen pulses performed at every 10% depth-of-discharge (DOD) increment, with an hour rest at open circuit at each increment to ensure that the battery has electrochemically equilibrated. Each discharge pulse is performed at the larger of either a 5C current or 25% of the manufacturer's maximum rated current.

A term known as the Battery Size Factor (BSF) is used to scale the remainder of the PNGV power- and energy-based tests. It is either obtained from the battery supplier or it may be calculated from the first series of HPPC tests. The BSF can also be utilized to estimate the unburdened cost, size, and weight of a full-size PNGV HEV battery. The calculation of the BSF is described in Reference 6.

Figure 1. Hybrid Pulse Power Characterization Profile



Self-discharge is calculated as the difference in capacity of a fully-charged battery compared to its capacity after sitting at open circuit for seven days. Cold cranking tests measure the battery's ability to provide three two-second 5 kW pulses at -30°C . Thermal performance is determined by repeating the static capacity and L-HPPC tests at various temperatures. Energy efficiency is determined using a charge-balanced pulse profile and calculating the ratio of watt-hours-output to watt-hours-input. EIS (i.e., full-spectrum complex impedance) measurements are made prior to the start of life testing, and then repeated when life testing is concluded.

Prior to commencing life testing, Reference Performance Tests (RPT's) are executed at 30°C to establish the baseline performance and then are repeated about every 25 days, thereafter. For Power Assist applications, the RPT's consist of a $C_1/1$ Constant-Current Discharge Test and a L-HPPC Test, and for Dual Mode applications, the RPT's include these two tests plus a 6-kW Constant-Power Available Energy Test.

End-of-testing for all life tests occurs when the device has completed the required time interval or number of cycles, or when it can no longer simultaneously meet the PNGV power and energy goals. For Power Assist applications, the cycle, pulse discharge power, and available energy goals are 300,000 cycles, 25 kW, and 300 Wh, respectively; and for Dual Mode these are 3,750 cycles, 45 kW and 1500 Wh, respectively. See Table 2.

Calendar-life testing is performed by bringing the battery to a prescribed SOC and temperature and holding at these conditions. Once each day, single discharge and regen pulses are applied

from which daily pulse resistances can be calculated.

Life cycling begins by bringing the device to the specified temperature and SOC conditions and performing an Operating Set Point Stability Test to ensure that a stable cycling condition has been established. Figure 2 shows the 25-Wh Power Assist Efficiency and Cycle-Life Profile. It consists of a discharge pulse and a regen pulse with interspersed rest periods. The cumulative length of a single profile is 72 seconds and constitutes one cycle, which is repeated continuously during testing.

Figure 2. Power Assist Efficiency and Cycle-Life Test Profile

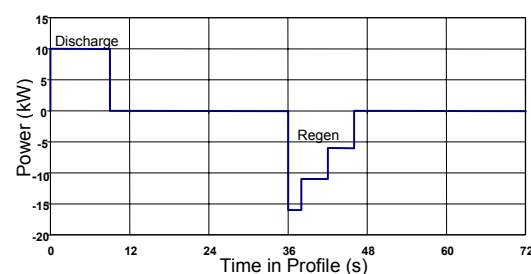
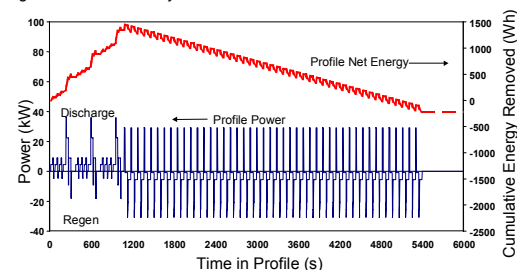


Figure 3 shows the Dual Mode Cycle-Life Test Profile and the corresponding Net Energy Profile. The power profile is composed of three Dynamic Stress Test (DST) pulse profiles followed by 45 recharge pulse profiles. The three DST profiles are scaled to 36 kW and have gross discharge of approximately 1500 Wh during this 18-minute sequence. The device is then returned to its initial charge condition using a 72-minute recharge profile sequence followed with a 10-minute rest, for a total duration of 1.667 hours per complete cycle.

Figure 3. Dual Mode Cycle-Life Test Profile



Accelerated Life Testing

Validation of battery performance with respect to the PNGV cycle-life and the calendar-life goals at normal HEV operating conditions is a lengthy process. Hence, national laboratories including

INEEL, SNL, and ANL have been investigating methodologies to accelerate both calendar-life and cycle-life testing. Typically, these developmental methodologies employ distributing ostensibly identical cells within a test matrix at various SOC's, temperature, and test profiles and then executing the test for prescribed periods of time. As with standard PNGV battery testing, the aging periods are interrupted periodically to execute RPT's from which cell performance as a function of time and the matrix variables may be ascertained. This data is then utilized to develop predictive models, typically utilizing an Arrhenius-based approach for temperature dependence, to extrapolate life predictions to normal operating conditions. Reports of INEEL's, SNL's, and ANL's work are found in Reference 5.

Abuse Tolerance Testing

Understanding the abuse tolerance characteristics of high energy and high power batteries is vital to the successful integration of such batteries in HEV's. A comprehensive array of tests has been developed and employed by SNL that enable vehicle developers to make sound decisions about the suitability of particular battery technologies; the need for protective packaging; and the controls required for energy storage system integration. The four principal abuse tolerance test categories are listed below and described further in Reference 8:

- Mechanical – includes mechanical shock, drop, penetration, rollover, immersion, and crush
- Thermal – includes radiant heat, thermal stability, thermal insulation, overheat, shock cycling, elevated temperature storage, and extreme cold temperature
- Electrical – includes short circuit, partial short circuit, overcharge, overdischarge, and AC current exposure
- Vibration – includes cyclical tests of varying amplitudes and frequencies.

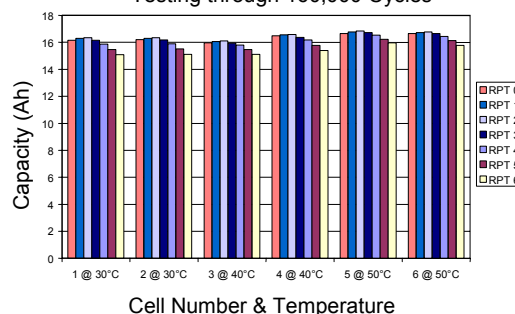
Analytical and Life Modeling Methodologies

Power fade (which is directly related to resistance growth) has been identified as a limiting factor for PNGV HEV batteries. Thus, testing and analytical assessments are largely focused on this parameter. Capacity fade is another key parameter that is tracked during cell testing.

Performance data from full-size, 12-Ah, lithium-ion, 2000-configuration Saft HP-12 cells are used as an example to show how PNGV performance parameters are calculated. Characterization testing was begun on these cells at the INEEL in December 2000. They then began life-cycle testing at 25% DOD in February 2001. Two cells each are being tested at 30°C, 40°C, and 50°C and to-date have successfully completed over 160,00 PNGV 25-Wh Power Assist life cycles.

The change in $C_1/1$ capacity with aging for the six cells is shown in Figure 4. As can be seen, the cells initially displayed a very slight increase in capacity with aging, but then began to monotonically decrease after about the third set of RPT's. After 160,000 cycles, the average capacity fade is 6.9% for the 30°C cells, 6.3% for the 40°C cells, and 4.7% for the 50°C cells. Interestingly, over the range tested the magnitude of the capacity fade decreases with increasing temperature for these cells.

Figure 4. Capacity Summary for Saft HP-12 Li-ion Cells from Beginning of Testing through 160,000 Cycles



The first step in determining the pulse power capability is to calculate the discharge and regen pulse resistances at each 10% DOD increment from the L-HPPC test data. Pulse resistance is simply the ratio of the change in the voltage divided by the change in current at specified times during selected pulses. Figures 5 shows the discharge and regen pulse resistance curves and the voltage curve versus DOD for one of the Saft cells at the beginning of testing (solid lines) and after 160,000 cycles (dashed lines) at 30°C. Note that as expected, the resistances increase with aging.

At each point in time, this information is used to calculate the discharge and regen pulse power capability. For example, the discharge pulse

power capability, P_{dis} , at each DOD is determined by:

$$P_{dis} = V_{min} (V_{OC} - V_{min}) / R_{dis}$$

where V_{min} is the manufacturer's specified minimum allowable voltage, V_{OC} is the open-circuit voltage immediately before the pulse begins, and R_{dis} is the corresponding discharge resistance. Each DOD can also be related to the corresponding amount of energy discharged to that point.

Figure 5. Soft Li-Ion Cell Pulse Resistances and Open Circuit Voltage at Beginning of Testing and After 160,000 Cycles

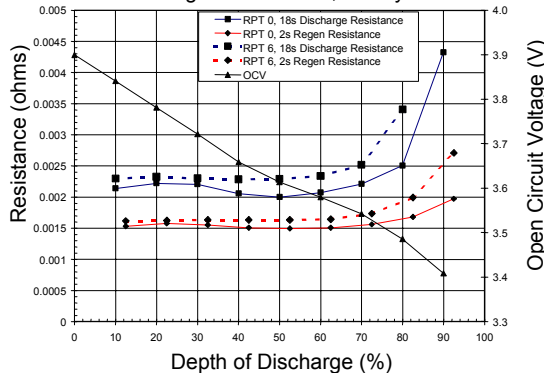
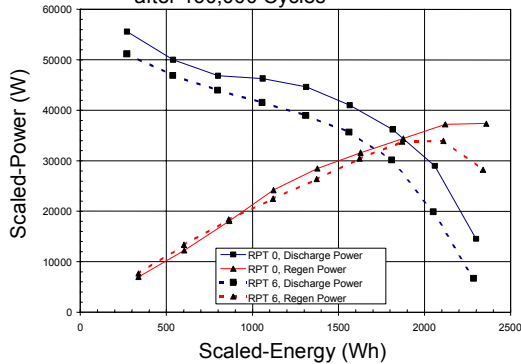


Figure 6 shows the corresponding discharge and regen pulse power curves versus energy for the same cell at the same two times in life. For these cells, the BSF was 44.3. That is, it was determined that 44.3 cells would be required to meet the PNGV power and energy goals for a full-sized automotive battery, and thus, individual cell values are multiplied by 44.3 to obtain Figure 6. Again as expected, the power capability decreases with cycling.

Figure 6. Soft Li-Ion Cell Pulse Power vs. Energy Removed at Beginning of Testing and after 160,000 Cycles



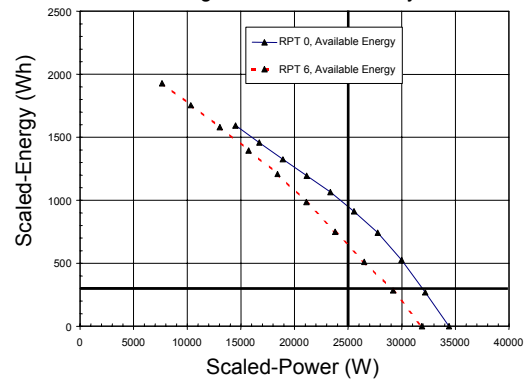
By calculating the difference in energy between the discharge power curve and the regen power curve, the available energy for the Power Assist mode is found as a function of power and is given by

$$E_{avail}(P) = E(P_{dis}) - E(P_{reg})$$

where $E(P_{dis})$ and $E(P_{reg})$ are the energies in Figure 6 associated with P_{dis} and P_{reg} , respectively.

The available energy as a function of power for this example is shown in Figure 7, again with a BSF of 44.3. [Note that the PNGV definition of available energy for the Dual Mode application is defined differently. For Dual Mode only, available energy is defined as the total energy released during a constant 6 kW discharge over the DOD range where the PNGV power goals can be met.]

Figure 7. Soft Li-Ion Cell Available Energy vs. Discharge Power at Beginning of Testing and after 160,000 Cycles

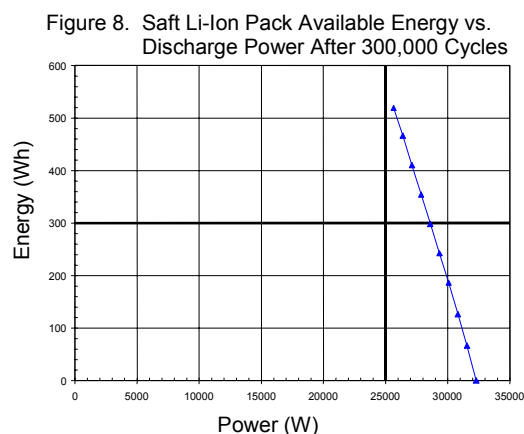


Also shown in Figure 7 are bold lines indicating the PNGV Power Assist energy goal of 300 Wh and the discharge pulse power goal of 25 kW. As the cell ages, the available energy decreases and the curves shift to the left. As long as the cell's available energy curves stay to the right of the crossover of the two goal lines, the cell is able to simultaneously meet the PNGV energy and power goals. Conversely, if the cell's available energy curve had moved to the left of this crossover point, the cell would no longer have met the goals and testing would have been stopped. For this example, after 160,000 cycles the cell is still well able to meet the power and energy goals, and linear extrapolation indicates that the cell will likely meet the PNGV Power Assist 300,000 cycle requirement, as well.

As a further example, performance data from a full-size 6-Ah, 280-V, lithium-ion Saft pack that has recently completed life-cycle testing at INEEL are shown in Figure 8. The Saft pack is comprised of six modules each containing twelve Saft HP-6 cells. The combination of these six modules with its associated hardware (the casing and the electronic control and thermal management systems) is generically referred to as a pack.

Characterization testing was begun on the pack at the INEEL in May 2000. It then began life-cycle testing at 30% DOD and 40°C and successfully completed the PNGV goal of 300,000 25-Wh Power Assist life cycles in November 2001. This device represents the most mature PNGV HEV battery technology.

At the beginning of cycling, the pack's PNGV pulse discharge power was about 33 kW and the available energy was about 620 Wh. And as shown in Figure 8, after completion of 300,000 cycles, the Saft pack was still able to exceed PNGV power and energy goals. At this point, the pack was able to provide 29 kW of discharge pulse power at the 300 Wh energy line and provided 590 Wh of available energy at the 25 kW line. Also, throughout testing, the pack maintained an energy efficiency around 96%.



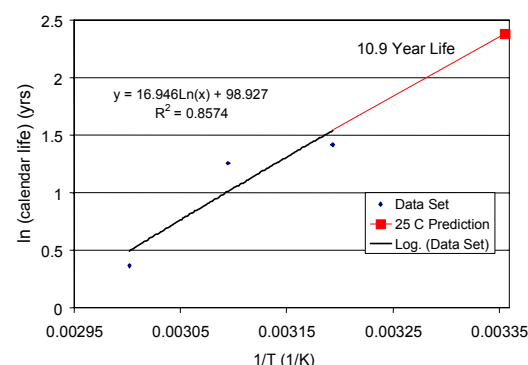
Life Modeling

Cell degradation as a function of calendar time or cycle count and other test conditions is being investigated at several national laboratories. From either the HPPC data collected during the RPT's or from the pulse data during calendar- and cycle-life testing, discharge and regen resistances can be calculated as a function of time and test conditions. This information is

being utilized to develop predictive life models for PNGV. Two distinct modeling approaches are being developed and evaluated by INEEL.

The first modeling approach is based upon the calculation of power fade over time as determined from the RPT's and associated available energy curves. Another set of six Saft 12-Ah lithium-ion HP-12 cells (1999 configuration) has been under test at INEEL for over 92 weeks using the PNGV calendar-life test. Two cells each are being subjected to temperatures of 40°C, 50°C, or 60°C. First, power fade as a function of time is calculated for each pair of cells at the three temperatures. This information can be used to construct an Arrhenius relation as shown in Figure 9, which enables extrapolation from the higher accelerated-aging temperatures to 25°C. The graph plots the natural logarithm of the "Years to End of Life" versus the inverse temperature in Kelvin and shows a projected calendar life of 10.9 years. Since the PNGV calendar-life goal is 15 years, battery developers are continuing their efforts to extend calendar life to meet the goal.

Figure 9 Calendar-Life Model for Saft HP-12 Li-Ion Cells.



Through participation in the ATD Program, INEEL has also developed a second modeling approach for both calendar life and cycle life. For example, a calendar-life model was developed to account for the time, temperature, and SOC of the batteries during testing (Ref. 9). The functional form of the model is given by:

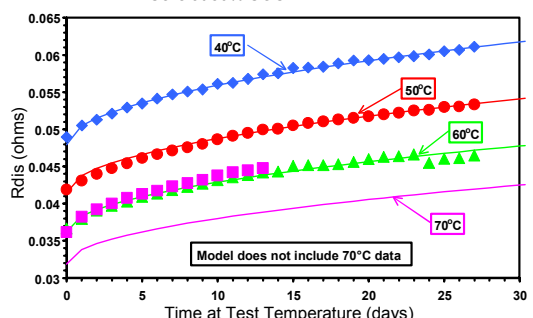
$$R(t, T, SOC) = a \{ \exp[b/T] \} t^{1/2} + c \{ \exp[d/t] \}$$

where a , b , c , and d are functions of SOC, and where b and d are related to activation energies, E_b and E_d , such that $b = E_b/R$ and $d = E_d/R$, and where R is the universal gas constant. (A similar approach has also been used to develop ATD cycle-life models (Ref. 10).)

The square-root-of-time dependence can be explained by either a one-dimensional diffusion type of mechanism, presumably of the lithium ions, or by a parabolic growth mechanism of a thin-film solid electrolyte interface (SEI) layer on the anode and/or cathode. A diffusion type of mechanism would arise from the diffusion of lithium ions into or out of the electrodes, through the electrolyte, through the separator, or through the SEI layer. The thickness of the SEI layer is believed to increase with aging and hence increase the cell's electrical resistance.

Figure 10 shows a representative comparison of ATD calendar-life test results to the model at 80% SOC. The model fit is excellent at 40°C, 50°C and 60°C, but not at 70°C, where it is believed that a different physical mechanism is controlling.

Figure 10. Calendar-Life Discharge Data and Model Predictions for ATD Cells at 80% SOC

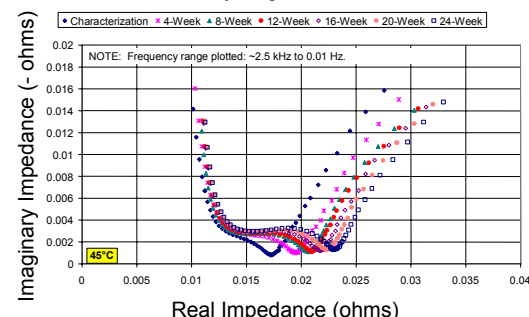


As part of the ATD Program, ANL and SNL are also developing life models. ANL is developing resistance growth models and ANL is utilizing data from their accelerated life testing to develop power and capacity fade models. The SNL modeling approach is based upon both linear and nonlinear regression analyses. A report of the ANL work is found in Reference 5 and that of SNL is found in Reference 11.

Others also are involved in modeling as reported in the OAAT-sponsored Workshop on Development of Advanced Battery Engineering Models. The topics discussed at the Workshop covered fundamental physical phenomena, thermal models, performance and economic models, and vehicle and power system simulation models. The workshop concluded with a discussion of data needs and sources. A report of the workshop is found in Reference 12.

Other new tools and methodologies are also being utilized at the national laboratories to investigate degradation mechanisms that may impact cell life. For example, Figure 11 shows an EIS Nyquist plot for a representative ATD lithium-ion cell cycled at 45°C for 24 weeks at INEEL. Increases in the real impedance as the cell ages are related to growth in the thin film SEI layer on the anode and/or cathode.

Figure 11. EIS for ATD Li-Ion Cells over 24 Weeks of Life Cycling

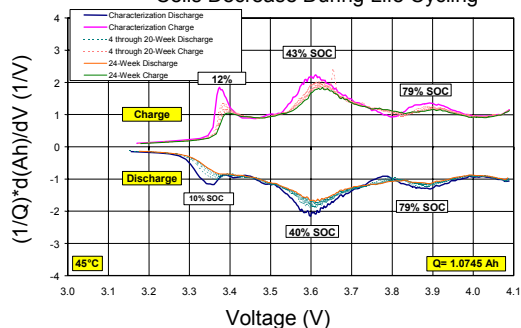


Lastly, a new measure of cell degradation under evaluation at the national laboratories is differential capacity, Q_{dif} , (Ref. 9 and 10). It is given by

$$Q_{dif} = (1/Q)[d(Ah)/dV]$$

where Q is the beginning-of-life (BOL) capacity and $d(Ah)/dV$ is the derivative of the capacity with respect to the voltage. Figure 12 shows a typical plot of differential capacity versus cell voltage calculated from a $C_{1/25}$ discharge and charge test for a representative ATD lithium-ion cell cycled at 45°C for 24 weeks at INEEL. Peaks are believed to be related to specific intercalation sites within the anode and/or cathode. The integrated area under each curve is equal to the BOL-normalized capacity of the cell. Thus, a decrease in the amplitude of a peak indicates that the cell's capacity has decreased over that respective voltage interval. It has been postulated that the degradation of cell performance with aging is related to both the changes in the amplitude and the location of these peaks. These changes may be a result of disruptions in the cathode crystalline lattice with aging.

Figure 12. Differential Capacity Peaks for Li-Ion Cells Decrease During Life Cycling



CONCLUSIONS

The OAAT and PNGV are investigating and funding the development of advanced high-power batteries for HEV applications. Under their auspices, new PNGV testing procedures and analytical methodologies have been developed. These enable the testing of various chemistries, technologies, and sizes of products and provide objective comparison of results. Also, calendar-life and cycle-life models are under development and evaluation at the national laboratories that enable the extrapolation of accelerated-aging test data to normal operating conditions. Recent performance data for Li-ion cells and packs show that PNGV power and energy cycle goals can be met and calendar life is approaching 10 years. Lastly, the national laboratories are continually exploring new testing and analytical methodologies to further aid the OAAT and PNGV to understand fundamental electrochemical degradation processes and to overcome technical barriers to the commercialization of lithium-ion batteries for HEV's.

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